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OXIDATION-RESISTANT METALLOCENES.
THE PREPARATION AND REACTIONS OF
DECACHLOROFERROCENE
AND DECACHLORORUTHENOCENE

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OXIDATION-RESISTANT METALLOCENES. THE PREPARATION AND REACTIONS OF DECACHLOROFERROCENE AND DECACHLORORUTHENOCENE

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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division, Air Force Materials Laboratory. The work was conducted under Project No. 7342, "Fundamental Research on Macromolecular Materials," Task No. 734201, "Basic Factors in the Synthesis of Macromolecular Materials." It was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. Harold Rosenberg as Project Scientist.

This report covers research conducted from May 1969 to October 1970.

This technical report has been reviewed and is approved.

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ABSTRACT

In order to obtain stable metallocenes, suitable for development into metal-containing polymers, resistant to oxidizing environments, the synthesis and reactions of the previously unreported class of perhalometallocenes was investigated. The detailed preparation of the first oxidation-stable metallocene, perchloroferrocene, i.e., 1, 1', 2, 2', 3, 3', 4, 4', 5, 5'-decachloroferrocene (I), by a stepwise metalation-exchange halogenation process, with and without ("direct") isolation of polychlorinated intermediates, is reported. The use of the "direct" route was extended to the synthesis of perchlororuthenocene (II) which was obtained from ruthenocene in six repetitive metalation chlorination steps. Attempts to prepare I or II by "sandwich"-type reactions, involving pentachlorocyclopentadiene or -dienides with iron or ruthenium salts, were unsuccessful.

Both I and II were found to be readily metalated by n-butyllithium in tetra-hydrofuran at low temperatures to yield the corresponding 1, 1'-dilithio deri-vatives. The versatility of these derivatives, as well as their precursors, for preparing other perchlorometallocenes, and particularly heteroannular difunc-tional monomers, is described. However, the use of perchlorometallocenes for the synthesis of perfluorometallocenes by exchange reactions with a metal fluoride failed to yield any fluorine-containing metallocenes.

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SECTION I

INTRODUCTION

A preliminary report of the preparation and properties of decachloro-ferrocene (Ie) the first metallocene completely substituted with electron-withdrawing groups and its polychlorinated precursors, Ia-Id, together with a thorough mass spectral analysis of Ie and its related polychlorinated ferrocenes, Ia-Ie and IIa-IIe, has recently appeared (References 1, 2, 3, and 4). The present report describes in detail the synthesis, reactions, and physical properties of these unique series of compounds, as well as those of the second perhalogenated metallocene, decachlororuthenocene (IIIa).
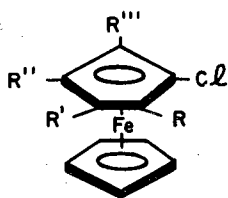
IIa. R, R', R'', R''' = H

IIb. R = Cl; R', R'', R''' = H

IIc. R, R' = Cl; R'', R''' = H

IId. R, R', R'' = Cl; R''' = H

IIe. R, R', R'', R''' = Cl
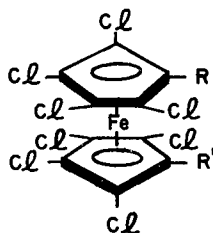
Ig. R, R' = Li

Ih. R, R' = I

Ii. R, R' = COOH

Ij. R = OCH₃, R' = Cl

Ik. R, R' = OCH₃

Iℓ. R = OC₂H₅, R' = Cl

Im. R, R' = OC₂H₅
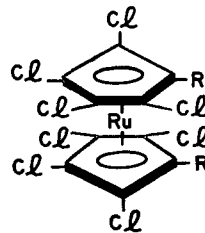
IIIa. R = Cl

IIIb. R = Li

IIIc. R = I

SECTION II

DISCUSSION

The preparation of decachloroferrocene (Ie) was carried out in a four-step synthesis as shown in Scheme 1, starting with 1,1'-dichloroferrocene (Ia) which is readily available by a recently developed procedure (Reference 5). The key to successive addition of chlorine to the ferrocene ring is the fact that chloro-ferrocene undergoes an alpha-proton abstraction upon reaction with n-butyl-lithium, in contrast to bromo- and iodoferrocene which undergo a metal-halogen exchange reaction with n-butyllithium (Reference 6). Heteroannular dilithiation of Ia was accomplished most conveniently with n-butyllithium as its N,N,N', N'-tetramethylethylenediamine (TMEDA) complex in hexane, and occurred, as anticipated, in the 2 and 2' positions to give If. Inverse addition of If to hexa-chloroethane (Reference 7) afforded 1,1',2,2'-tetrachloroferrocene (Ib) in good yield. Subsequent lithiation steps were carried out with n-butyllithium in tetrahydrofuran (THF) due to the low solubility of compounds Ib-Ie in hexane. Thus, by dilithiation, followed by exchange chlorination, Ib was converted to 1,1',2,2',3,3'-hexachloroferrocene (Ic), Ic was converted to 1,1',2,2',3,3', 4,4'-octachloroferrocene (Id), and Id was converted to 1,1',2,2',3,3',4,4', 5,5'-decachloroferrocene (Ie).

The yields of Ic and Id decreased sharply as a result of the formation of by-products in each step which were exceedingly difficult to remove from the main product. Although these by-products were not isolated and definitively identified, their GLC behavior indicated that they were probably starting ma-terial, monochlorinated starting material, and higher chlorinated starting ma-terial. The yield of these by-products was increased markedly by direct addi-tion of the hexachloroethane to the lithiated intermediate. Increase of the re-action time did not noticeably decrease the amount of monochlorinated starting material, but led only to lower overall yields. From this evidence, it appears that both the monochlorinated and unchlorinated starting materials were formed as shown in Scheme 2.

SCHEME 1
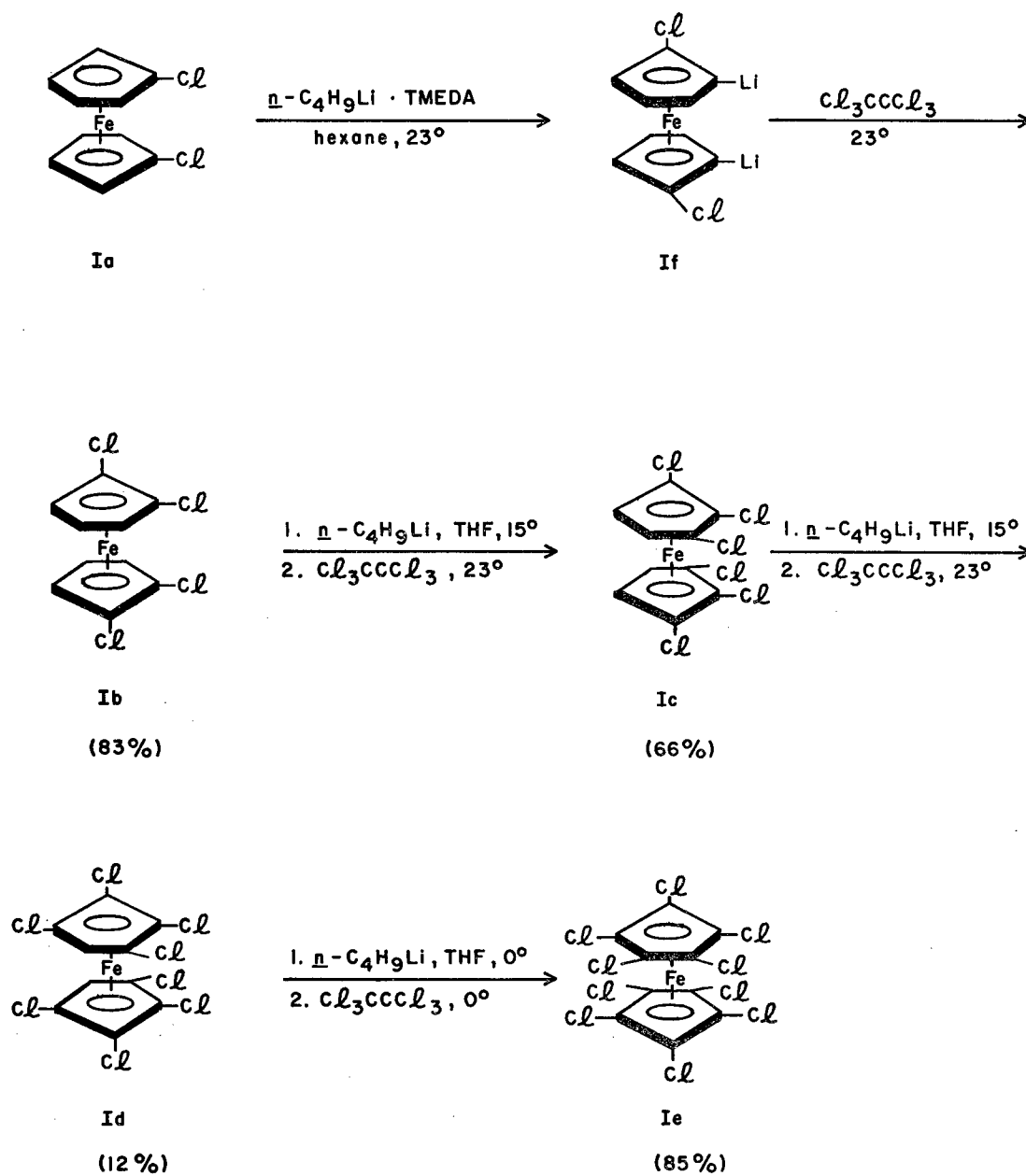
SCHEME 2
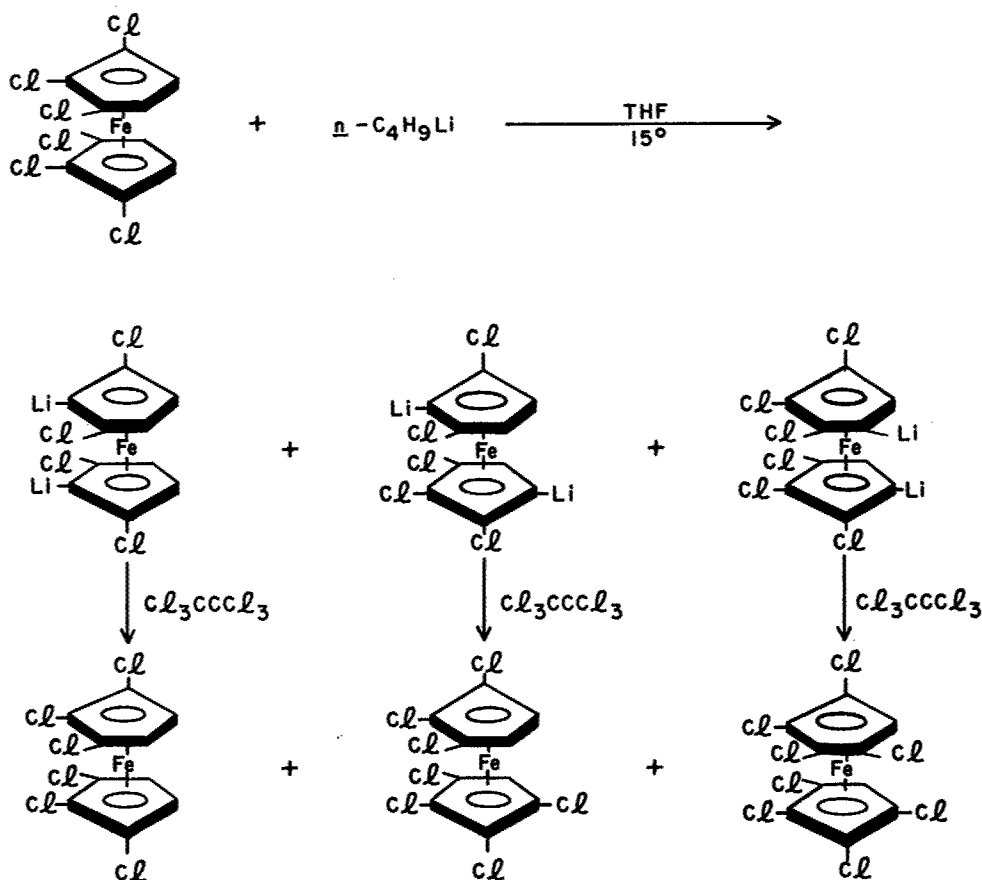
When a chlorine atom on a metallocene ring is flanked by one or more additional chlorine atoms, it becomes activated sufficiently so that metal-halogen exchange becomes competitive with hydrogen abstraction. A competition of this type has previously been reported for 1, 2, 3-trichlorobenzene and 1, 2, 3, 4-tetrachlorobenzene in reactions with n-butyllithium (Reference 8). The small amounts of more highly chlorinated by-products are undoubtedly due to abstraction of more than two protons from the starting material. The similarity of all of these by-products to the desired product probably accounts for their resistance to removal by recrystallization.

As a result of the low yields obtained in the synthesis of Ic and Id, the overall yield of decachloroferrocene was only 7%. On the assumption that the by-products removed from the intermediates at each step of the synthesis were

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themselves chlorinated ferrocenes, Ia was also converted to Ie without purifying
the intermediates. Five lithiation-chlorination reactions afforded a 42% overall
yield of Ie, making this procedure the preferred route to Ie.

A modification of the above direct route from Ia to Ie was also found appli-
cable to the synthesis of decachlororuthenocene (IIIa) from ruthenocene. A
total of seven successive lithiation-chlorination reactions were used, with com-
plex mixtures of products resulting in each of the early reactions. The degree
of polylithiation and metal-halogen exchange occurring during the lithiation half
of these reactions appeared to be much greater than that observed with the fer-
rocene system. This suggests that the only convenient way of isolating the
intermediate chlorinated ruthenocenes would be by means of preparative GLC.
The yield of IIIa (based on ruthenocene) was 14%. In considering alternate
synthesis for perchlorometallocenes it would appear that the most desirable
route to either Ie or IIIa would be via a one-step "sandwiching" of a polychlo-
rinated cyclopentadienide. Two previous attempts to form Ie by reacting fer-
rous chloride with either pentachlorocyclopentadienyllithium or the corresponding
Grignard (Reference 9) have been reported. The failure of these attempts is
probably due to the low reactivity of the pentachlorocyclopentadienyl anion. We
were equally unsuccessful in trying to react pentachlorocyclopentadienyllithium
with either ferrous iodide or ferrous acetylacetonate, as well as in attempting
to react pentachlorocyclopentadiene with diethylamine and ferrous acetylaceto-
nate. In a study of reactions of the perchlorometallocenes it was found that
both Ie and IIIa underwent heteroannular dilithiation upon reaction with n-butyl-
lithium to give Ig and IIIb, respectively. These versatile intermediates, in
turn, provide synthetic routes to a variety of substituted perchloroferrocenes
and perchlororuthenocenes. As examples, Ig was hydrolyzed to give Id, was
reacted with iodine to give 1,1'-diiodooctachloroferrocene (Ih), and was car-
bonated to give octachloroferrocene-1,1'-dicarboxylic acid (Ii). IIIb was simi-
larly reacted with iodine to give 1,1'-diiodooctachlororuthenocene (IIIc).

Direct nucleophilic substitution of Ie was also carried out. Reaction of Ie
with sodium methoxide afforded both methoxynonachloroferrocene (Ij) and 1,1'-
dimethoxyoctachloroferrocene (Ik), with the relative amounts of each dependent
upon reaction time. Sodium ethoxide reacted with Ie to form not only ethoxy-
nonachloroferrocene (Il) and 1,1'-diethoxyoctachloroferrocene (Im) but also a

mixture of isomers containing three and four ethoxy groups. GLC indicated the presence of two triethoxy isomers and three tetraethoxy isomers.

In contrast to Ie, the methoxy and ethoxy derivatives were very soluble in all common solvents, making their purification very difficult. Only Im was obtained in sufficient purity to afford a satisfactory elemental analysis. However, the mass spectra of all of these compounds afforded molecular ion peaks with the calculated isotopic distributions. The expected metal-ring fragmentation was also present for each compound. The location of the second ethoxy or methoxy group in the 1' position in compounds Ik and Im was shown by the absence of a $(M - C_5Cl_5)^+$ peak. Similarly, a distribution of two ethoxy groups per ring in the mixture of tetraethoxy isomers was indicated by the absence of either $M^+-C_5Cl_5$ or $M^+-C_5Cl_4OC_2H_5$ peaks, and a distribution of two ethoxy groups in one ring and one in the other in the mixture of triethoxy isomers was indicated by the absence of either $M^+-C_5Cl_5$ or $M^+-C_5Cl_2(OC_2H_5)_3$ peaks. We may thus conclude that the three tetraethoxy isomers are the 1,1',2,2'-; the 1,1',2,3'-; and the 1,1',3,3'-isomers, while the triethoxy isomers must be the 1,1',2- and 1,1',3- isomers.

Attempts to prepare decafluoroferrocene or decafluororuthenocene by an exchange reaction involving treatment of Ie or IIIa with cesium fluoride were unsuccessful. Efforts to react cesium fluoride with either Ih or IIIc were equally unfruitful.

The synthesis of the homoannularly polychlorinated derivatives, IIb - IIe, was carried out by a procedure analogous to that used for the preparation of Ib-Ie, as outlined in Scheme 3. No attempt was made to optimize yields in any of the four cases.

SCHEME 3 IIa
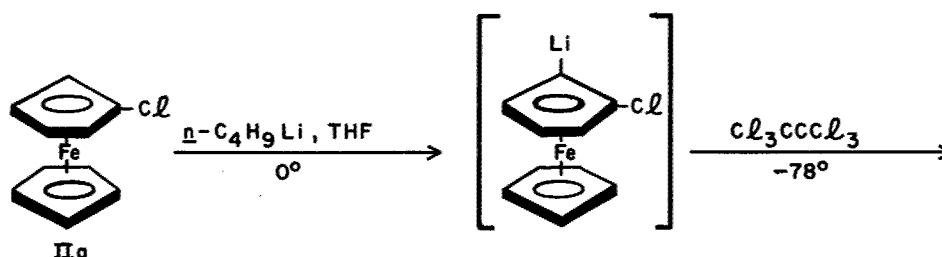
SCHEME 3 IIb through IIe (Cont'd)

IIb   IIc

IId   IIe
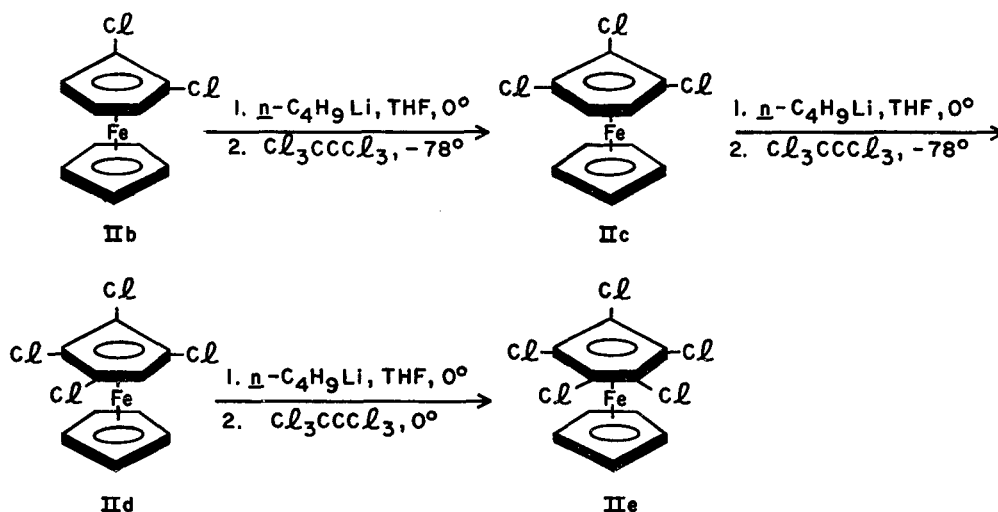
The primary evidence for the structures proposed for the two series of polychlorinated ferrocenes, Ib-Ie and IIb-IIe, was obtained from satisfactory elemental analyses, GLC analyses, mass spectral analyses, and the nmr spectra of the compounds. GLC (on SE-30 silicone rubber columns) showed an approximately incremental increase in retention time with increasing chlorine content for the compounds of each series. A thorough analysis of the mass spectra of these compounds has been given in a separate publication (Reference 4) and will not be presented in detail here. The molecular ion peaks, isotopic distributions, and fragmentation patterns were all in accord with the proposed structures. The most interesting fragmentation pathway was via the elimination of $FeCl_2$, suggesting a possible intramolecular fulvalene formation.

While the mass spectral fragmentation patterns show the distribution of the chlorine atoms between the rings, the distribution of the chlorine atoms within the rings cannot be ascertained. This latter information, however, can be obtained from the nmr spectra of the compounds. The nmr absorbance peaks for compounds Ia-Ie, IIa-IIe, and ferrocene are given in Table I. These figures substantiate the prediction that lithiation will occur in a position alpha to a chlorine atom. For compounds Id and IId it can be seen that there is a marked downfield shift in the absorbance of the lone proton in the substituted ring or rings. This proton must necessarily be flanked by a chlorine atom on each side in these two compounds. This observation, coupled with the fact that the

TABLE I

NMR ABSORBANCE PEAKS

(Values are given in cps from TMS as internal standard in $CDCl_3$)			
Compound	Unsubstituted Ring	α-Protons	β-Protons
Ia	–	263, 265, 267	246, 248, 250
Ib	–	264, 267	245, 248, 251
Ic	–	265	–
Id	–	275	–
Ie	–	–	–
IIa	250	260, 261.5, 263	238, 240, 242
IIb	255	260, 263	235, 238, 241
IIc	257	259	–
IId	262	284	–
IIe	263	–	–
Ferrocene	246	–	–

center of alpha proton absorbance does not vary for compounds Ia-Ic and IIa-IIc, is firm evidence that each of the substituted ring protons in Ib, Ic, IIb, and IIc is flanked by a single chlorine atom. Such a situation can only exist if the chlorine atoms are all located adjacent to one another. The integration ratio and multiplicity of each proton absorbance is also in accord with the proposed structures in every case.

Also of interest in the NMR spectra is the lack of significant variance in the position of the beta proton absorbance in Ia-Ib and IIa-IIb. These findings suggest that protons alpha to a chlorine atom are influenced only by electron-withdrawing inductive effects to a degree dependent upon the number of alpha chlorine atoms. On the other hand, no negative inductive influence, but only a positive resonance effect is exerted upon protons beta to a chlorine atom. This resonance effect is completely superseded by the inductive effect of an alpha chlorine atom, and only shows up in the absence of alpha chlorine atoms.

SECTION III

EXPERIMENTAL

1. General

All reactions were carried out under an atmosphere of high purity nitrogen (99.99%). n-Butyllithium in hexane was obtained from Foote Mineral Co., and was found by titration to be 1.5 Molar. Chloroferrocene was prepared by a procedure reported in Reference 10, from ferroceneboronic acid, and was purified by preparative GLC. Ruthenocene was prepared by a reported procedure and purified by recrystallization from methanol. GLC analyses were performed on either an F&M Model 500 gas chromatograph using 2 ft x 1/4 in. O.D. columns packed with 10% SE-30 silicone rubber on Chromasorb P, or an F&M Model 402 gas chromatograph using 4 ft x 1/8 in. O.D. glass columns packed with 5% SE-30 gum rubber on Chromosorb P. Molecular weight determinations were carried out on all compounds except Ii with a CEC Model 21-1108 mass spectrometer. Chlorine isotope distributions obtained for the ferrocene derivatives, and chlorine-ruthenium isotope distributions obtained for the ruthenocene derivatives were all in agreement with the calculated isotopic patterns. For those compounds for which an exact mass determination was not made, the correct nominal mass was obtained for all peaks in the molecular ion cluster.

2. 1,1',2,2'-Tetrachloroferrocene (Ib)

A solution of 1,1'-dichloroferrocene (Reference 5) (15.7 g, 0.0616 mole) in hexane (900 ml) was stirred at 23° while a solution of n-butyllithium in hexane (100 ml, 0.15 mole) was added, followed by the addition of TMEDA (18.6 g, 0.16 mole). The reaction mixture was stirred at 23° for 50 minutes and then added over a 35-minute period to a stirred solution of hexachloroethane (47 g, 0.20 mole) in hexane (300 ml). After addition was complete, stirring was continued for 5 minutes and the reaction mixture was filtered through a bed of alumina. The filtrate was concentrated to dryness and the residue was fractionally sublimed. After removal of hexachloroethane at 45° (0.25 mm), the product was sublimed at 120-125° (0.25). The sublimate weighed 16.55 g and

consisted (by GLC analysis) of trichloroferrocene (2%) and 1,1',2,2'-tetrachloroferrocene (98%). The latter represents an 83% yield of Ib. Recrystallization from hexane afforded 1,1'2,2'-tetrachloroferrocene of mp 147°. Anal. Calcd for $C_{10}H_6Cl_4$ Fe: C, 37.09; H, 1.87; Cl, 43.80; Fe, 17.25; mol wt ($^{35}Cl_3$ ^{37}Cl isotopes), 323.8543. Found: C, 37.10, 36.87; H, 1.74, 1.91; Cl, 43.86, 43.71; Fe, 17.46, 1721; mol wt, 323.8519.

3. 1,1',2,2',3,3'-Hexachloroferrocene (Ic)

A solution of 1,1'2,2'-tetrachloroferrocene (7.73 g, 0.0238 mole) in dry THF (700 ml) was stirred at 15° while a solution of n-butyllithium in hexane (100 ml, 0.15 mole) was added. The reaction mixture was stirred for 2.5 hours at 15° and then added over a 20-minute period to a solution of hexachloroethane (48 g, 0.20 mole) in hexane (400 ml). After addition was complete, stirring was continued for five minutes and the reaction mixture was filtered through a bed of alumina. The filtrate was concentrated to dryness and the residue was fractionally sublimed. The product weighed 8.83 g and consisted (by GLC analysis) of pentachloroferrocene (7%), 1,1',2,2',3,3'-hexachloroferrocene (92.5%) and heptachloroferrocene (0.5%). Recrystallization from hexane afforded 6.17 g (66%) of 1,1',2,2',3,3'-hexachloroferrocene of mp 191°. Anal. Calcd for $C_{10}H_4Cl_6$ Fe: C, 30.58; H, 1.03; Cl 54.17; Fe, 14.22; mol wt ($^{35}Cl_5$ ^{37}Cl isotopes), 391.7764. Found: C, 31.03, 30.97; H, 1.03, 1.03; Cl, 53.65, 53.78; Fe, 14.87, 14.92; mol wt, 391.7755.

4. 1,1',2,2',3,3',4,4'-Octachloroferrocene (Id)

The experimental procedure used was the same as described above for 1,1',2,2',3,3'-hexachloroferrocene, except that lithiation was carried out for only 1.5 hours. From 1.40 g of 1,1',2,2',3,3'-hexachloroferrocene there was obtained 1.28 g of material which consisted (by GLC analysis) of hexachloroferrocene (1.5%), heptachloroferrocene (15%), 1,1',2,2',3,3',4,4'-octachloroferrocene (79%), nonachloroferrocene (3%), and decachloroferrocene (1.5%). Recrystallization from hexane afforded 0.19 g (12%) of 1,1',2,2',3,3',4,4'-octachloroferrocene of mp 212°.

Anal. Calcd for $C_{10}H_2Cl_8$ Fe: C, 26.02; H, 0.44; Cl, 61.45; Fe, 12.10; mol wt ($^{35}Cl_6$ $^{37}Cl_2$ isotopes), 461.6955. Found: C, 26.23, 26.09; H, 0.57, 0.52; Cl, 16.90, 61.84; Fe, 11.91, 11.92; mol wt 461.6933.

5. Decachloroferrocene (Ie)

    a. From octachloroferrocene

A solution of 1,1'-2,2',3,3',4,4'-octachloroferrocene (0.584 g, 0.00126 mole) in dry THF (130 ml) was stirred at 0° while a solution of n-butyllithium in hexane (2.5 ml, 0.0037 mole) was added. The reaction mixture was stirred at 0° for one hour and then hexachloroethane (2.37 g, 0.010 mole) was added. Stirring was continued for fifteen minutes and the reaction mixture was then filtered through a bed of alumina. The filtrate was concentrated to dryness and dry-column chromatography of the residue (hexane as eluent) afforded 0.623 g of material which consisted (by GLC analysis) of octachloroferrocene (1%), nonachloroferrocene (8%) and decachloroferrocene (91%). This mixture was dissolved in carbon tetrachloride and stirred with concentrated nitric acid for 29 hours. The carbon tetrachloride layer was then passed through a column of alumina to give 0.565 g of decachloroferrocene (85%) of mp 245-246° (dec). Anal. Calcd for $C_{10}Cl_{10}$ Fe: C, 22.64; Cl, 66.83; Fe, 10.53; mol wt ($^{35}Cl_8$ $^{37}Cl_2$ isotopes), 529.6175. Found: C, 22.82, 22.85; Cl, 66.31, 66.32; Fe, 9.75, 9.72; mol wt, 529.6120.

    b. From 1,1'-Dichloroferrocene - Direct Method

1,1'-Dichloroferrocene (Reference 5) (17.47g, 0.0686 mole) in hexane (1500 ml) was stirred at 23° while a solution of n-butyllithium in hexane (133 ml, 0.20 mole), followed by TMEDA (23g, 0.20 mole), was added. The reaction mixture was stirred at 23° for 1 hour and then cooled to -70°. Hexachloroethane (71g, 0.30 mole) was added, and the temperature was allowed to rise to 10° over a 1-hour period. The reaction mixture was then extracted with water, and the hexane layer separated and concentrated to dryness. The hexachloroethane was removed by sublimation and the crude residue was reacted with n-butyllithium (200 ml, 0.30 mole) in dry THF (1000 ml) at 0° for 3 hours. The reaction mixture was cooled to -70°, and hexachloroethane (95 g, 0.40 mole)

was added. The temperature was allowed to rise to 5° over a 1-hour period, and the reaction mixture was then passed through a column of alumina (THF as eluent). The solvent was distilled from the eluate at 23° in vacuo and the hexachloroethane removed by sublimation. The residue was subjected to the above described (lithiation-halogenation) reaction in THF and the accompanying workup procedures three more times, the sole modification being a decrease in the lithiation time to 2.5 hours, 60 min, and 30 min for the final three runs. The crude product from the last reaction, after removal of hexachloroethane by sublimation was recrystallized from hexane to give 13.0 g of Ie of 98% purity by GLC. The residue from the mother liquor was stirred with a mixture of carbon tetrachloride-concentrated nitric acid for 5 hours and chromatographed on alumina to give an additional 2.2 g of Ie of 98% purity (by GLC). The total amount (15.2g) thus obtained represents a 42% yield of Ie.

6. Decachlororuthenocene (IIIa)

A solution of ruthenocene (Reference 11) (11.55g., 0.0500 mole) in hexane (1000 ml) was stirred and heated at reflux while a solution of n-butyllithium in hexane (115 ml, 0.15 mole) was added. Heating was discontinued and TMEDA (22 ml, 0.15 mole) added at a rate which maintained reflux. The reaction mixture was refluxed for 1 hour and then cooled to -20°. Hexachloroethane (47.4 g, 0.20 mole) was added and the temperature was allowed to rise to 10° over a 30-min period. After removal of the solids present by filtration, the hexane filtrate was passed through a column packed with alumina. Hexachloroethane was eluted with petroleum ether, and the mixture of chlorinated ruthenocenes eluted with carbon tetrachloride. The crude mixture, after removal of solvent, was subjected to the same reaction as described above, except that lithiation was carried out at 23° instead of at reflux temperature. The crude product obtained was dissolved in THF (500 ml) and stirred at -70° while a solution of n-butyllithium in hexane (200 ml, 0.30 mole) was added. The reaction mixture was warmed to 0° over a 30-min. period, stirred at 0° for 2 hours, and cooled to -70°. Hexachloroethane (95 g, 0.40 mole) was added, and the temperature was allowed to rise to 10° over a 1-hour period. The entire reaction mixture was then absorbed on alumina, and the THF removed by evaporation. Dry-column chromatography was carried out on the dried alumina to remove hexachloroethane upon elution with petroleum ether and to afford a crude

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mixture of chlorinated ruthenocenes upon elution with carbon tetrachloride. This mixture was subjected to the above-described reaction in THF four more times with the following lithiation temperatures/lithiation times: 0°/1 hr; 0°/1 hr; -70°/30 min; -70°/30 min. The product from the final reaction was recrystallized from heptane to give 4.2 g (14%) of IIIa of 99% purity (by GLC). The material showed some evidence of sublimation above 300° and decomposed at 360-365°. <u>Anal.</u> Calcd for $C_{10}Cl_{10}Ru$: C, 20.86; Cl, 61.58. Found: C, 20.88, 20.76; Cl, 61.80, 61.77. The molecular ion cluster was a unique and complex pattern from 566 to 586 mass units, which was identical with the pattern calculated for the compound.

7. Attempted "Sandwiching" Preparations of Ie

A solution of pentachlorocyclopentadienyllithium prepared from hexachlorocyclopentadiene (13.6 g, 0.050 mole) and n-butyllithium (33 ml, 0.050 mole) was reacted with ferrous iodide (3.1 g, 0.010 mole) at -70°. The reaction mixture was warmed to 5° over a 45-min period, and passed through a bed of alumina (with methylene chloride as eluent). The solvent was removed, and the residue extracted with hot heptane. Chromatography on alumina of the heptane extracts yielded none of the desired metallocene but only pentachlorocyclopentadiene together with its dimer. Similar results were obtained when the pyridine complex of ferrous acetylacetonate (Reference 12) was used in place of the ferrous iodide. When a mixture of pentachlorocyclopentadiene (Reference 13), diethylamine, and ferrous acetylacetonate was refluxed in pyridine, followed by the same workup described above; again, no trace of the desired metallocene was observed.

8. Lithiation and Hydrolysis of Decachloroferrocene

A solution of decachloroferrocene (0.411 g, 0.000774 mole) in dry THF (75 ml) was cooled with liquid nitrogen until frozen. A solution of n-butyllithium in hexane (2.0 ml, 0.0030 mole) was added, and the reaction mixture was allowed to warm, with stirring, over a 15-minute period to -40°. Distilled water (2 ml, 0.09 mole) was added, giving a voluminous white precipitate, and stirring was continued for 10 minutes while the mixture was allowed to warm to 0°.

The mixture was then filtered and the filtrate concentrated to dryness. Dry-column chromatography of the residue on alumina afforded 0.359 g (100%) of material which consisted (by GLC analysis) of pure 1,1',2,2',3,3',4,4'-octa-chloroferrocene (GLC retention time, mp and infrared spectrum identical with those of an authentic sample).

9.   1,1'-Diiodooctachloroferrocene (Ih)

A suspension of decachloroferrocene (1.00 g, 0.00190 mole) in dry diethyl ether (175 ml) was stirred at -70° while a solution of n-butyllithium in hexane (3.8 ml, 0.0057 mole) was added. After 30 min at -70°, an orange solution was present. Continued stirring for 30 min more afforded a voluminous precipitate. Iodine (2.54 g, 0.010 mole) was added, and the reaction mixture was warmed to 5° over a 40-min period. Passage through a bed of alumina (methylene chloride as eluent) followed by removal of solvent afforded 1.35 g. (99%) of Ih 98% purity by GLC. Recrystallization from hexane gave mp 240° (dec with evolution of I_2). <u>Anal.</u> Calcd for $C_{10}Cl_8I_2Fe$: C, 16.83; Cl, 39.75; I, 35.57; Fe, 7.82. Found: C, 16.83, 16.74; Cl, 39.54, 39.63; I, 35.27, 35.41; Fe, 8.01, 7.96.

10.   Octachloroferrocene-1,1'-dicarboxylic Acid (Ii)

A solution of decachloroferrocene (0.80 g, 0.00151 mole) in dry THF (125 ml) was stirred at -70° while a solution of n-butyllithium in hexane (3.0 ml, 0.0045 mole) was added. The resultant deep orange solution was stirred at -70° for 10 min and then excess dry ice was added. The reaction mixture was stirred for 20 min. while warming to 0°, and then poured into 500 ml of water and extracted 3x200 ml with hexane. The aqueous layer was acidified with 10% HCl, affording a voluminous precipitate which was collected, washed with water, and dried to give 0.81 g (97%) of Ii, mp 245° (dec), after recrystallization from THF-benzene. <u>Anal.</u> Calcd for $C_{12}H_2O_4Cl_8Fe$: C, 26.22; H, 0.36; Cl, 51.60; Fe, 10.16. Found: C, 26.12, 26.37; H, 0.31, 0,34; Cl, 51.39, 51.36; Fe, 10.48, 10.43. The IR spectrum (KBr) showed an intense C=0 band at 1680-1695 cm^{-1}.

11. 1,1'-Diiodooctachlororuthenocene (IIIb)

A solution of decachlororuthenocene (0.70 g, 0.0012 mole) in dry THF (125 ml) was stirred at -70° while a solution of n-butyllithium in hexane (2.4 ml., 0.0036 mole) was added. After stirring at -70° for 15 min, iodine (2.0 g, 0.0080 mole) was added and the reaction mixture was warmed to 10° over a 40-min period. Passage through a bed of alumina followed by removal of solvent left 0.89 g (98%) of IIIb. After recrystallization from hexane, the material showed sublimation above 300°, darkening above 325°, and iodine elimination above 350°. <u>Anal.</u> Calcd for $C_{10}Cl_8I_2Ru$: C, 15.70; I, 33.19; Ru, 13.21. Found: C, 16.06, 15.83; I, 32.72, 32.71; Ru, 12.71, 12.73. The mass spectrum of the compound, analogously to that of IIIa, afforded a "fingerprint" pattern identical with the calculated pattern.

12. Reaction of Decachloroferrocene with Sodium Methoxide

A mixture of decachloroferrocene (0.21 g, 0.00040 mole) and sodium methoxide (0.5 g, 0.01 mole) in methanol (125 ml) was stirred and refluxed for 18 hr. Repeated analysis of the reaction mixture during this period was carried out by thin layer chromatography (TLC) on silica gel with CCl_4 as developer. A steady decrease in the intensity of the starting material (R_f=0.85) was noted, accompanied by the formation of two new compounds of R_f=0.62 and R_f=0.40, respectively. The formation of the latter compound appeared to be much slower than that of the former at first, but the ratio of intensities of the latter to the former compound increased with time. After 18 hr, the reaction mixture was cooled, absorbed on alumina, and chromatographed on alumina. Two bands were eluted with CCl_4, but separation was poor. Subsequent re-chromatography on silica gel afforded good separation of the two bands. The material from the first band weighed 0.15 g (72%) and was determined by mass spectrometry to be methoxynonachloroferrocene (Ij). The material from the second band weighed 0.06 g (28%) and was determined by mass spectrometry to be 1,1'-dimethoxyoctachloroferrocene (Ik). Both methoxy derivatives were very soluble in all common solvents, and we were unable to effect complete purification for elemental analysis.

13. Reaction of Decachloroferrocene with Sodium Ethoxide

To a solution formed by dissolving sodium metal (0.80 g, 0.035 mole) in absolute ethanol (175 ml) was added decachloroferrocene (1.00 g, 0.00190 mole), and the resultant mixture was stirred and refluxed for 59 days. At intervals during the reaction, samples were withdrawn and analyzed by TLC, GLC, and mass spectrometry. The following times and percentages (determined by GLC) of starting material, monoethoxy, diethoxy, triethoxy, and tetraethoxy derivatives were obtained: 1 hr, 2, 95, 3, 0, 0; 4 hr, 0, 50, 50, 0, 0; 6 hr, 0, 25, 75, 0, 0; 43 hr, 0, 0, 65, 30, 5; 117 hr, 0, 0, 23, 60, 17; 208 hr, 0, 0, 4, 73, 23; 384 hr, 0, 0, 0, 76, 24. After 59 days (1416 hr) the reaction mixture was cooled, absorbed on silica gel, and chromatographed. CCl_4 eluted two bands from which were obtained 0.192 g (28%) of triethoxyheptachloroferrocene as an oil and 0.480 g (72%) of tetraethoxyhexachloroferrocene as an oily solid. GLC of the triethoxy derivative showed two isomers of which the relative percentages in order of increasing retention time were 83 and 17%. GLC of the tetraethoxy derivative showed three isomers of which the relative percentages in order of increasing retention time were 59, 36, and 5%.

A second reaction was carried out under the same conditions as described above, using 0.10 mole of sodium ethoxide. The reaction mixture was worked up after 6 hr to give 0.81 g (67%) of 1,1'-diethoxyoctachloroferrocene (Im) and 0.27 g (22%) of triethoxyheptachloroferrocene. The Im was recrystallized from a small volume of hexane to give mp 107-108°. Anal. Calcd for $C_{14}H_{10}O_2Cl_8Fe$: C, 30.59; H, 1.83; Cl, 51.59; Fe, 10.16. Found: C, 30.60, 30.46; H, 2.21 2.29; Cl, 51.30; Fe, 10.13.

14. Attempted Preparations of Decafluoroferrocene

Decachloroferrocene was heated with excess (~50:1) cesium fluoride in sulfolane at 100° for 24 hr to give no reaction. When the temperature was raised to 145°, gradual decomposition took place. At 190°, decomposition was very rapid.

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1,1'-Diiodooctachloroferrocene was heated with excess cesium fluoride in sulfolane at 155-160° for 20 min. Extensive decomposition occurred, and only a small amount of material was obtained from column chromatography. Mass spectrometric analysis indicated the eluate to consist of octachloroferrocene, iodooctachloroferrocene, and butyliodooctachloroferrocene, the last named possibly being formed by breakdown of the sulfolane.

15. Attempted Preparation of Decafluororuthenocene

Decachlororuthenocene and excess cesium fluoride were heated in sulfolane at 240° for 1 hr to give a 50% recovery of starting material after column chromatography.

Gradual decomposition also occurred upon heating 1,1'-diiodooctachlororuthenocene and excess cesium fluoride in sulfolane at 190°.

16. 1,2-Dichloroferrocene (IIb)

A solution of chloroferrocene (4.42 g, 0.0200 mole) in dry THF (125 ml) was stirred at 0° while a solution of n-butyllithium in hexane (30 ml, 0.045 mole) was added. The reaction mixture was stirred at 0° for 1.5 hours and then cooled at -78°. A solution of hexachloroethane (14.2 g, 0.060 mole) in hexane (50 ml) was added, and the reaction mixture was then allowed to warm to 0° over a 30-min period. Subsequent workup consisted of dry-column chromatography on alumina with hexane as eluent. The excess hexachloroethane eluted first, followed by a yellow band from which, after solvent removal, there was obtained 3.48 g of material consisting (by GLC analysis) of 1,2-dichloroferrocene (81%) and a material (19%) determined (by mass spectral analysis) to be a trichloroferrocene. Recrystallization from methanol afforded 1,2-dichloroferrocene of mp 88-90° (lit* mp 88.5-90°). Anal. Calcd for $C_{10}H_8Cl_2$ Fe: C, 47.11; H, 3.16; mol wt 253.9351. Found: C, 47.39, 47.22; H, 3.14, 3.05; mol wt 253.9355.

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*Reference 14

17. 1, 2, 3-Trichloroferrocene (IIc)

The experimental procedure used was the same as described above for
1, 2-dichloroferrocene. From 4.50 g of 1, 2-dichloroferrocene, there was
obtained 5.12 g of material which consisted (by GLC analysis) of 1, 2-dichloro-
ferrocene (3%), 1, 2, 3-trichloroferrocene (86%) and tetrachloroferrocene (11%).
Recrystallization from methanol afforded 1, 2, 3-trichloroferrocene of mp
103.5-104.5°. <u>Anal.</u> Calcd for $C_{10}H_7Cl_3$ Fe: C, 41.51; H, 2.44; mol wt
287.8961. Found: C, 41.57, 41.46; H, 2.47, 2.42; mol wt 287.8982.

18. 1, 2, 3, 4-Tetrachloroferrocene (IId)

The experimental procedure used was the same as described above for
1, 2-dichloroferrocene. From 0.70 g of 1, 2, 3-trichloroferrocene, there was
obtained 0.62 g of material which consisted (by GLC analysis) of 1, 2, 3-trichloro-
ferrocene (10%), 1, 2, 3, 4-tetrachloroferrocene (80%), and pentachloroferrocene
(10%). Preparative GLC afforded 1, 2, 3, 4-tetrachloroferrocene of mp 81-82°.
<u>Anal.</u> Calcd for $C_{10}H_6Cl_4$ Fe: C, 37.09; H, 1.87; mol wt ($^{35}Cl_3{}^{37}Cl$ isotopes),
323.8543. Found: C, 37.38, 37.12; H, 1.86, 1.98; mol wt, 323.8559.

19. 1, 2, 3, 4, 5-Pentachloroferrocene (IIe)

A mixture of 1, 2-dichloroferrocene (25%) and 1, 2, 3-trichloroferrocene
(75%) was subjected to the reaction procedure described above for 1, 2-dichloro-
ferrocene to give a material consisting of 1, 2, 3-trichloroferrocene (42%),
1, 2, 3, 4-tetrachloroferrocene (29%), and pentachloroferrocene (29%). Repe-
tition of the reaction with this mixture afforded a material consisting of 1, 2, 3,
4-tetrachloroferrocene (42%), and 1, 2, 3, 4, 5-pentachloroferrocene (58%),
together with a small amount of hexachloroferrocene. This mixture was re-
acted in dry ether with excess <u>n</u>-butyllithium-hexane solution, followed by addi-
tion of hexachloroethane at 0°. Dry-column chromatography afforded a mix-
ture of tetrachloroferrocene (20%), 1, 2, 3, 4, 5-pentachloroferrocene (70%), and
hexachloroferrocene (10%). Recrystallization from methanol afforded 1, 2, 3,
4, 5-pentachloroferrocene of mp 143-144°. <u>Anal.</u> Calcd for $C_{10}H_5Cl_5$ Fe: C,
33.52; H, 1.41; mol wt ($^{35}Cl_4{}^{37}Cl$ isotopes) 357.8154. Found: C, 33.25,
33.53; H, 1.41, 1.45; mol wt 357.8144.

SECTION IV

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13. ABSTRACT

   In order to obtain stable metallocenes, suitable for development into metal-containing polymers, resistant to oxidizing environments, the synthesis and reactions of the previously unreported class of perhalometallocenes was investigated. The detailed preparation of the first oxidation-stable metallocene, perchloroferrocene, i.e., 1,1',2,2',3,3',4,4',5,5'-deca-chloroferrocene (I), by a stepwise metalation-exchange halogenation process, with and without ("direct") isolation of polychlorinated intermediates, is reported. The use of the "direct" route was extended to the synthesis of perchlororuthenocene (II) which was obtained from ruthenocene in six repetitive metalation chlorination steps. Attempts to prepare I or II by "sandwich"-type reactions, involving pentachlorocyclopentadiene or -dienides with iron or ruthenium salts, were unsuccessful.

   Both I and II were found to be readily metalated by $\underline{n}$-butyllithium in tetra-hydrofuran at low temperatures to yield the corresponding 1,1'-dilithio derivatives. The versatility of these derivatives, as well as their precursors, for preparing other perchlorometallocenes, and particularly heteroannular difunctional monomers, is described. However, the use of perchlorometallocenes for the synthesis of perfluorometallocenes by exchange reactions with a metal fluoride failed to yield any fluorine-containing metallocenes.

14. KEY WORDS	LINK A		LINK B		LINK C	
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Decachlororuthenocene						
Oxidation-resistant metallocenes						